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CATALYSTS ON THE OXIDATION OF KEROSENE

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Introduction

The oxidation of kerosene, in the course of which various secondary products such as hydroxy acids and their esters (lactones, lactides, and estolides) are prepared, is a very complicated catalytic process. Problems in the catalytic oxidation of low-boiling liquid petroleum hydrocarbons have not yet been investigated to a satisfactory degree. The knowledge available on the catalytic oxidation of solid petroleum hydrocarbons is only indirectly applicable to these problems.

Past experiments have shown that the ordinary salts of acids - for example, the metallic salts of naphthenic or other organic acids - are acceptable oxidation accelerators [1]. Nevertheless, neither has the role of a cation in such a catalyst been defined, nor has the organometallic compound most suitable for producing secondary products been determined. Therefore, it is necessary to discover the catalyst which will promote the formation of the complicated secondary products (the various polyatomic hydroxy acids and their esters) directly from the primary compounds.

For this purpose, experiments were conducted in which various organometallic salts were examined.

According to data available from scientific literature [2], the most active quasi-heterogeneous catalysts are those compounds in which naphthenic acids - obtained in the purification of kerosene fractions - are present as the anion.

Experimental Part

In this study the author used naphthenic acids (with the number 218.3) which were free from unsaponified organic material and mineral salts. Chromium, manganese, iron, cobalt, copper, barium, and tin cations were studied.

Chemically pure organic salts of these metals, prepared by the ordinary method, were dissolved in the kerosene to obtain solutions of different concentrations. Only the cation itself and its concentration were variable factors in the experiments. All other factors - the kerosene, oxidation time, temperature, consumption of air, conditions of introducing the catalyst, etc. - were kept constant.

The author arrived at the following conclusions:

1. Neither the valence, nor the atomic number, nor the atomic weight of the metals determine the degree of their activity as cations in the oxidation of kerosene. Nor is the relationship of these three factors to the properties of the acids and esters known.

2. Mn is the most active cation of the seven studied. Fe and Co are also active, but causes the formation of a sludge from the desired reaction products. Cr is slightly less active, and after a certain point an increase in the amount of Cr has no further effect either in accelerating or retarding the reaction. Pb and Ba are much less active that Cr, Mn, Fe, and Co; and Cu is not at all active. An active catalyst in the sense used here was previously defined [3] as one which will promote an increased yield of these acids and esters.

As can be noted from the graph in the Appendix, all six of the active cations except Pb and Cr have well-defined optimum concentration points on their parabolic curves.

3. The ration of the optimum concentrations of the cations of active catalysts is approximately equal to the ratio of their atomic weights.

The author, a member of the Central Scientific Research Laboratory of "Neftemaslo" Plant, Glavtrest, Submitted his paper 5 Sept 49.

Appendix

The results of Tsyskovskiy's study are presented in two tables and a graph as shown below:

Table 1

Properties of the acids and esters produced at the optimum concentration of the cation.

Cation	sp gr	Viscosity (in Engler seconds)*	Acid number (in mg KOH)	Molecular weight	Remarks
Mn	1.072	58.84	75.0	280	The acids and esters are brown, there is no sludge.
Fe	1.037	122.36	68.	315	The products are thick and black in color. A lot of sludge is formed.
Co	1.078	84.3	67.5	322	No sludge. Products a light red color.
Pb	1.048	29.1	92.	275	

*Northern European unit used with the Engler Viscometer.

Table 2

Relationship of the Atomic Weights and Optimum

Concentrations of Cations.

Cation	Atomic weight	Ratio of atomic weights	Experimentally found optimum concentration of the cation	Theoretical optimum concentrations (According to that observed for Mn)	Ratio of the optimum concentrations of the metal in the catalyst
Mn	54.93	1	0.091	0.091	1.0
Fe	55.85	1.017	0.0953	0.0925	1.045
Co	58.94	1.073	0.1	0.0976	1.05
Pb	207.21	3.772	0.336	0.348	3.69

Caption for Graph on pg. 755 [see original document available in FDD Library]:

Oxidation of kerosene in the presence of various cations.

A - concentration of the catalyst (in % of the metal by weight).

B - yield of esters and acids in percent by weight.

Cations indicated numerically as follows: 1 - Pb, 2 - Ba, 3 - Cr, 4 - Mn, 5 - Fe, 6 - Co

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2. Tsyskovskiy, Oxidation of Petrolatum and Paraffin, Gostoptekhizdat, 1948.
3. Tsyskovskiy, Zhurnal Prikladnoy Khimii, 5, 1948.

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